



Reduced phosphorus retention by anoxic bottom sediments after the remediation of an industrial acidified lake area: Indications from P, Al, and Fe sediment fractions

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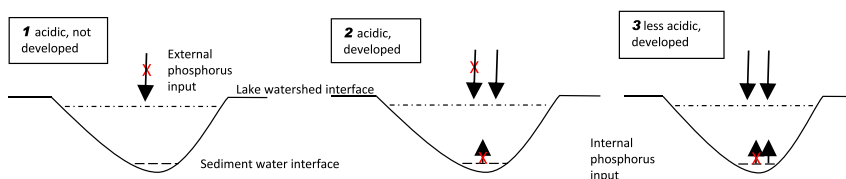
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HIGHLIGHTS

- Reduced P retention by anoxic bottom sediments of an acidified, developed lake
- Causes of increased eutrophication and cyanobacteria include internal P loading.
- P, Al, and Fe sediment fractionations indicate decreased P adsorption capacity.
- 0–5, 5–10 cm sediment fractionation of 2 sites in acid lake and in 2 comparison lakes
- Formerly acidified, remediated sediment shows characteristics of P releasing sediments.

GRAPHICAL ABSTRACT

Phases during the recuperation of (mining-induced) acid lakes



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ABSTRACT

Formerly acidified lakes and watersheds can become more productive when recovering from acidity, especially when exposed to anthropogenic disturbance and increased nutrient loading. Occasional toxic cyanobacterial blooms and other signs of eutrophication have been observed for a decade in lakes located in the Sudbury, Ontario, mining area that was severely affected by acid deposition before the start of smelter emission reductions in the 1970s. Oligotrophic Long Lake and its upstream lakes have been exposed to waste water input and development impacts from the City of Greater Sudbury and likely have a legacy of nutrient enrichment in their sediment. Based on observations from other published studies, we hypothesized that P, which was previously adsorbed by metals liberated during acidification caused by the mining activities, is now being released from the sediment as internal P loading contributing to increased cyanobacteria biomass. Support for this hypothesis includes (1) lake observations of oxygen depletion and hypolimnetic anoxia and slightly elevated hypolimnetic total P concentration and (2) P, Al, and Fe fractionation of two sediment layers (0–5, 5–10 cm), showing elevated concentrations of TP and iron releasable P (BD-fraction), decreased concentrations in fractions associated with Al, and fraction ratios indicating decreased sediment adsorption capacity. The comparison with two moderately enriched lakes within 200 km distance, but never directly affected by mining operations, supports the increasing similarity of Long Lake surficial sediment adsorption capacity with that of unaffected lakes. There is cause for concern that increased eutrophication including the proliferation of cyanobacteria of formerly acidic lakes is wide-spread and occurs wherever recovery coincides with anthropogenic disturbances and physical changes related to climate change.

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1. Introduction

Many regions have been affected by acidifying gasses produced during the industrial revolution in Europe (e.g., Czech Republic, East Germany, Italy, and Sweden) and North America (Adirondacks, western and eastern United States; Central Ontario, Canada) as well as in more recently developed and developing countries in Asia and South America (e.g., copper smelters, <https://www.thebalance.com/the-20-largest-copper-refineries-2339744>). Much effort has been put into the remediation of such landscapes, including emission control and the liming of waterbodies and catchment soils (Lydersen et al., 2002; Manca et al., 2016).

Over 7000 lakes were acidified to the point of biological damage in a 17,000 km² area in the vicinity of the City of Greater Sudbury, Ontario, where acidification was produced by emissions from metal smelters associated with large mining operations (Keller, 2009). Large-scale emission control programs at the Sudbury smelters in the 1970s and 1990s achieved overall reductions of ~90% in sulphur and metal emissions in comparison to peak emission levels in the 1960s (Keller, 2009). These emission reductions were accompanied by pro-active remediation efforts including the liming of soils and water in the affected area that has initiated a slow biological and chemical recovery of area lakes (Yan et al., 2016).

Water transparency in the mining-affected Sudbury lakes was high when productivity was curtailed by acidity, metal toxicity, and impoverishment in nutrients and organic matter (Yan, 1983; Yan et al., 1996). Recent signs of recovery include increases in alkalinity, pH, nutrient concentration (especially of phosphorus, P), and organic matter measured as dissolved organic carbon (DOC) (Table 1), which has led to increased productivity and phytoplankton biomass and decreased transparency (Keller et al., 2007). Finally, increased eutrophication has led to incidences of cyanobacteria blooms in Sudbury area lakes since 2008 (https://www.sdhc.com/wp-content/uploads/2015/07/Blue-Green-Algae_Identified_From_2006_To_Present_Compliant.xlsx; downloaded Aug 4, 2017). Cyanobacterial blooms in these formerly low-nutrient lakes are startling, and it is important to examine their causes, because there are no easy and well-established measures to treat and prevent their manifestations once they occur regularly (Lürling et al., 2015).

Metal accumulation in catchment soils and lake sediments controls P retention capacity. Lakes in poorly buffered watersheds and acid lakes are typically nutrient poor which has been attributed to the scavenging of phosphate by hydroxides of aluminum (Al), iron (Fe) and other metals (Kopáček et al., 2005; Norton et al., 2006). From previous work by Kopáček et al. (2015) and Norton et al. (2006) we discern several

phases in the eutrophication of mining-associated, formerly acid lakes that we test in the Sudbury area (Fig. 1). The hypothesized phases are based on the changing P retention capacity of catchment soils and lake bottom sediments. P retention capacity is mainly determined by aluminum hydroxides, the lakes' current acid recovery status (based on the lakes' and surroundings' former exposure to mining emissions), their hydrological setting, and their P load.

1.1. Hypothesized phases during the recovery of acidic lakes impacted by mining

Phase 1. High emissions of acidifying pollutants during active mining operations: Less developed lakes during mining have little external P input because (a) Al keeps P bound in the catchment soils and (b) there is not much anthropogenic input. They also have only limited amount of releasable sediment P. Lakes are ultra-oligotrophic without internal P loading.

Phase 2. High emissions of acidifying pollutants during active mining with increasing development: In anthropogenically disturbed lakes during mining, Al keeps P bound in the catchment soils except for direct developmental P input and land-use change (increased external P load). Al hydroxides adsorb P in the water column and settle P to the lake bottom sediment, where it accumulates. Lakes are still oligotrophic without discernable internal loading.

Phase 3. Recovery and acidity-related restoration with reduced acid emissions and continuing development: Declining ionic Al leaching in catchment soils does not prevent P export. Decreased Al hydroxides in the water column (caused by decreased Al leaching from

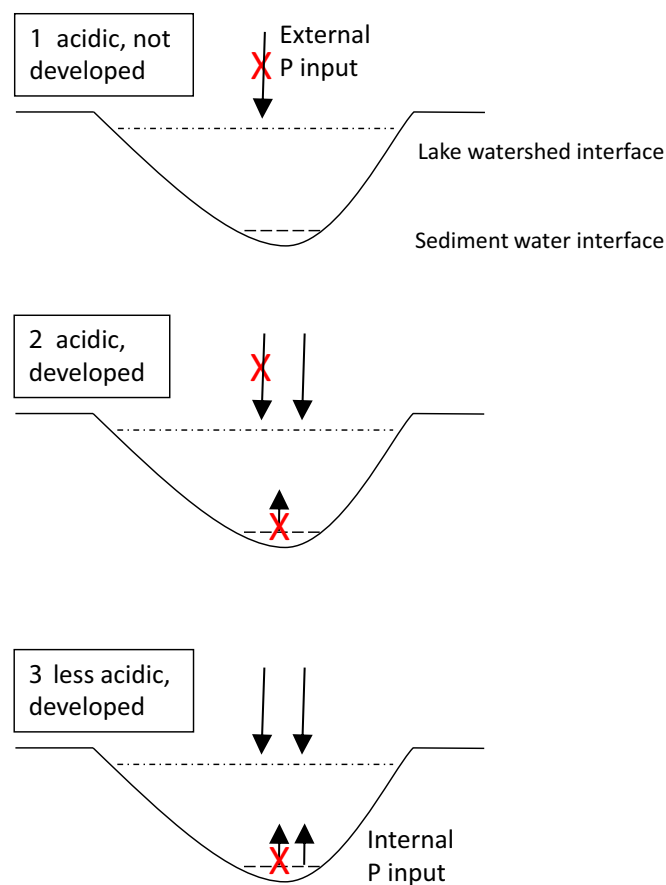


Fig. 1. Hypothesized stages in the eutrophication of acid lakes. During emissions of acidifying pollutants Al compounds in the catchment soils generally diminish external P loading; Al in the sediment prevents internal load as sediment P release (red x).

Table 1

Comparison of 1990 with 2003 summer water quality variables in composite samples of the mixed surface layer (epi- and metalimnion) of lakes in the Long Lake watershed. Source: Appendix 1 of Keller et al. (2004).

Lake	Year	pH	Alkalinity (as mg/L CaCO ₃)	Al (μg/L)	DOC (mg/L)	TP (μg/L)
Clearwater	1990	4.9	−0.85	130	0.5	<2
	2003	6.3	1.19	16	2.9	5
Lohi	1990	4.9	−0.69	130	1.1	<2
	2003	6.3	2.57	22	3.4	9
Daisy Lake	1990	4.8	−0.88	360	na	2
	2003	6.2	2.02	30	2.0	9
Richard	1990	7.3	17.61	<20	na	2
	2003	7.3	21.85	6	2.8	12
Silver	1990	4.3	−2.90	860	<0.3	<3
	2003	6.0	0.87	14	2.4	7
Tilton	1990	5.8	0.84	<40	2.5	<8
	2003	6.3	2.63	17	2.6	7
McFarlane	1990	7.1	31.68	<50	3.8	10
	2003	7.3	33.72	8	4.6	18
Long	1990	6.9	13.79	<20	3.4	<5
	2003	7.1	16.83	14	4.1	8

catchment soils) permits only limited binding of lake P. Newly settled P includes organic P forms that are diagenetically transformed and accumulate as P adsorbed onto iron oxy-hydroxides in the surface sediment, causing some internal loading during hypolimnetic hypoxia. Sediment released P can support cyanobacterial blooms. In this phase, lakes are on a trajectory of becoming meso- and then eutrophic.

P retention was enhanced by Al and P interactions in many nutrient-poor, oligotrophic non-calcareous lakes in the Appalachian Mountains of New York and Maine (Norton et al., 2006), as well as in central European lakes exposed to acid-deposition (Kopáček et al., 2000), (Phase 1 and 2, Fig. 1). While P liberation concurrent with Al solubilization in the catchment soils is possible during periods of increased flushing and decreased pH, adsorption processes reverse the process during transfer to downstream lakes (Reinhardt et al., 2004; Norton et al., 2006).

Phase 3 is implied in a conceptual scheme developed by Kopáček et al. (2015) for central European mountain lakes recovering from atmospheric acidification. Kopáček et al. (2015) suggest that in such lakes “the elevated P availability in the lakes results from (1) increasing terrestrial export of P accompanying elevated leaching of DOC and decreasing phosphate-adsorption ability of soils due to their increasing pH, and (2) decreasing in-lake P immobilization by Al hydroxide due to decreasing leaching of ionic Al from the recovering soils”, which leaves more P in the lake partially associated with dissolved organic acids or retained as Fe oxy-hydroxides and releasable under anoxic conditions in the sediments. A decrease in exchangeable Al concomitant with an increase in pH in forest catchment soils affected by past acidification in the northeastern USA and Eastern Canada was recently substantiated (Lawrence et al., 2015).

To determine whether lakes in the Sudbury area have entered Phase 3, we specifically examined sediment from a higher order lake affected by past mining activities (Fig. 2). We examined two sediment layers at two locations in multi-basin Long Lake, where the layers represent past (5–10 cm) and more recent (0–5 cm) conditions with respect to exposure to mining and development influences (Section 2.3).

Content and concentrations of total sediment P, Fe, and Al do not necessarily indicate sediment adsorption characteristics because totals include inert fractions, although in some studied lakes sediment TP or TFe:TP ratios were related to P release (Nürnberg, 1988; Jensen et al., 1992). But elemental fractions after specific extractions (Jan et al., 2013) and their various proportions and ratios were found to be related

to P retention and anoxic P release, especially in non-calcareous surficial sediments (Kopáček et al., 2005; Lake et al., 2007).

To determine differences in the P adsorption property of the sediment layers, we compared the concentration of several Al, Fe, and P species and investigated their proportions or ratios. We then compared the established ratios to specific thresholds developed in several published studies (Kopáček et al., 2000; Lake et al., 2007), below which Al species are not high enough to prevent anoxic P release from iron oxy-hydroxides. Further, we compared our sediment ratios to those observed after Al-based lake restoration treatments to determine changes in the sediment P fraction permanently adsorbed by Al hydroxides (Rydin et al., 2000; Huser, 2017).

In addition to two sites in Long Lake, Sudbury, we conducted a similar sediment analysis in two non-acidified lakes. Both, Three Mile and Brandy Lake were about 200 km south of Sudbury, but still on the Precambrian Shield (Fig. 2). All study lakes had been exposed to seasonal and permanent development on their shores and had experienced cyanobacteria blooms in recent years despite comparably low trophic state in Long Lake (oligotrophic, according to trophic state classification of Nürnberg, 1996) and Hammell's Bay of Three Mile Lake (oligo-mesotrophic). Brandy Lake is a meso-eutrophic lake with a slightly acidic pH caused by humic and fulvic acids as indicated by a comparably high DOC concentration. Three Mile Lake pH has been above neutral since monitoring began in 1990 (also, Table 2). While the concentration of sediment Al species is likely highest in formerly acid Long Lake, we expect that the interactions between Al hydroxides and P are similar, albeit influenced by different chemical characteristics including high DOC concentrations in coloured Brandy and elevated TP concentrations in both non-mining lakes.

2. Material and methods

2.1. Limnological characteristics, cyanobacteria, and internal P loads of study lakes

2.1.1. Long Lake in the mining-affected, Sudbury area

Most of Long Lake and its watershed is located within the City of Greater Sudbury, Ontario, a region that has been severely affected by acid deposition. Consequently, and similar to other area lakes, Long Lake has historically been relatively clear and nutrient-poor, with low apparent phytoplankton biomass, despite enhanced nutrient loading

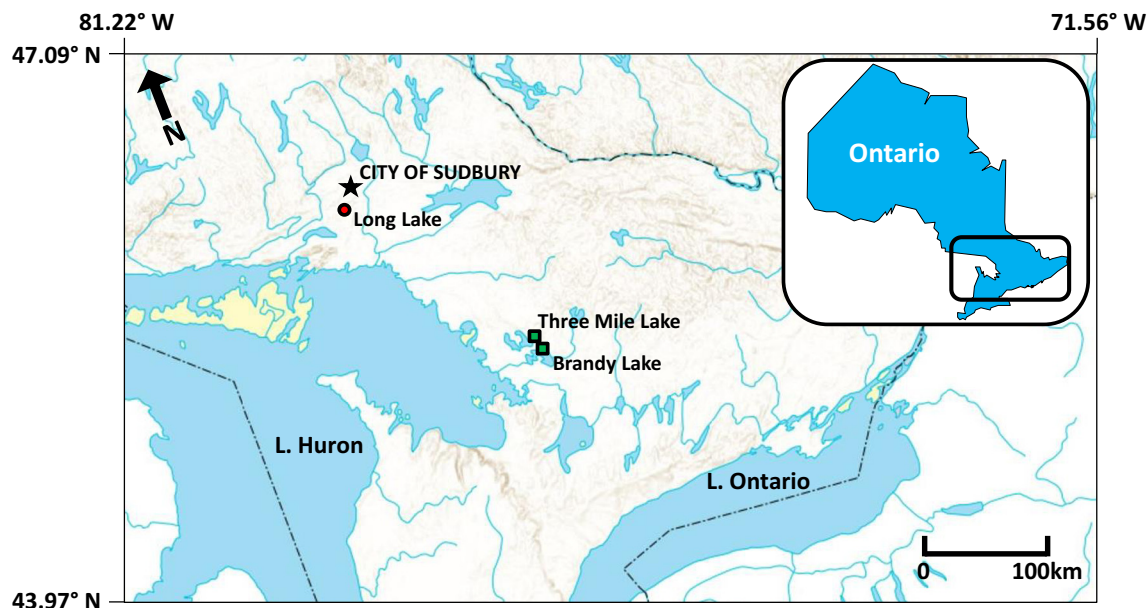


Fig. 2. Location of the study lakes, with Long Lake closest to the Sudbury mining area. For maps of the individual lakes and coring locations see Fig. S1.

Table 2

Morphometric, hydrological and chemical characteristics of the study lakes. Epilimnetic values unless stated otherwise.

Characteristics	Long	Brandy	Hammell's Bay of Three Mile
Approximate location (Lat, Long)	46.36, −81.1	45.10, −79.5	45.17, −79.5
Total Watershed Area, Ad (km ²)	108.06	39.85	13.20
Surface Area, Ao (km ²)	8.65	1.08	2.30
Ratio of areas Ad/Ao	12.49	36.90	5.74
Maximum Depth, z _{max} (m)	36.50	7.50	12.00
Mean Depth, z (m)	7.53	3.52	6.68
Volume (10 ⁶ m ³)	65.20	3.80	15.49
Morphometric ratio, z/Ao, (m/km ²)	2.56	3.39	4.40
Annual flushing rate (per yr)	0.86	5.54	0.51
Annual water load (m/yr)	6.50	19.49	3.43
Spring TP (μg/L)	8.3 ^a	32.6	14.5
Jun-Sep average TP (μg/L)	5–8 (Table 1)	24.5	14.5
Nitrate (μg/L) (early summer 2015)	55 ^b	46	2
DOC (mg/L)	4.8 ^c	11.8	4.7
Ca (mg/L) (early summer 2015) ^c	7.6	2.8	4.8
Sulfate (mg/L) (early summer 2015) ^c	8.0	1.9	2.6
pH (early summer 2015) ^c	7.1	6.7	7.1
Hypolimnetic pH (at date of coring)	6.8	n.a.	6.8

n.a., Not available.

^a 6.8–10.0 μg/L, n = 9, 2002–2014.

^b Compares to 1990 value of 90 μg/L (Keller et al., 2004).

^c Epilimnetic value measured on day of coring.

from long-term urban development. Long Lake's watershed to lake surface area ratio is relatively large (Table 2), indicating that upstream areas have a large influence on its water quality. There are at least 6 tributaries contributing to Long Lake from at least 10 upstream lakes. In this watershed, TP concentration was higher in 2003 compared to 1990, with two lakes (Richard and McFarlane) reaching TP levels above 10 μg/L (Table 1).

Connected, rapidly flushing lakes with bedrock that yields low to intermediate alkalinity water interspersed by peatlands showed the greatest improvement in pH and acid neutralizing capacity of lakes in the Sudbury mining region (Nriagu et al., 1998). Due to its large watershed that includes 8–9% of wetland and a relatively fast flushing rate (Table 2), resulting in a relatively high buffering capacity and DOC concentration by 1990 (Table 1), Long Lake recovered from acidity more rapidly than many other lakes in the region, but other impairments, above all high nutrient loading, are becoming more prominent. Long Lake catchment soils almost certainly have a legacy of nutrient enrichment from years of anthropogenic development and land use changes in southern Sudbury. Increased P export upon remediation and recovery of these soils may be contributing to eutrophication including cyanobacterial blooms in Long Lake and its feeder lakes. Such eutrophication can be expected because acidification does not alter or destroy basic limnological functions of lakes (Nriagu et al., 1998). The signs agree with Keller's conceptual model of anticipated changes during biological recovery of acidified lakes (Keller et al., 2007) and are confirmed by observations of long-term residents (Long Lake Association Members, personal communication 2015).

Biological signs of recuperation from acidification in regional lakes include the recovery of scaled chrysophyte assemblages in upstream Daisy and neighboring Swan lakes, shown by a decline in acidophilic taxa and an increase in circum-neutral taxa in recently deposited lake sediments (Tropea et al., 2010).

Besides decreased water transparency, there are more direct signs of increased phytoplankton in Long Lake and upstream McFarlane Lake. Both lakes experienced cyanobacteria blooms in 7 years between 2008 and 2016 (<https://www.sdhc.com/alerts/blue-green-algal-blooms-reported-big-lake-long-lake>). The Aug-Sep and Oct-Nov blooms in 2008 consisted of the cyanobacteria *Leptolyngbya*, *Phormidium*,

Dolichospermum (formerly *Anabaena*), and *Cylindrospermum* (Evans and Saleh, 2015).

The low water TP concentration (Table 1) makes it analytically difficult to determine small P increases. But slightly elevated TP concentrations coincide with hypolimnetic hypoxia which supports the possibility of redox-related P release in several of Long Lake's basins (Fig. S2). Besides morphometric influences (Nürnberg, 1995), hypolimnetic hypoxia in Long Lake is likely enhanced by anthropogenic nutrient and organic loads, a trend that exists globally (Jenny et al., 2016).

2.1.2. Comparison lakes

The sediment of two softwater lakes (Hammell's Bay of Three Mile Lake, and Brandy Lake), located approximately 19 km apart and about 180 km south of Long Lake, were investigated for comparison. Their watersheds consist primarily of glacial deposits of sand, silt and clay with some organic deposits over granitic bedrock. The Three Mile catchment straddles the remnant basin of glacial Lake Algonquin so that its watershed soils are generally deeper and more fertile than is typical for the Muskoka region. The watersheds of both lakes include wetlands and forest, with some development (15% wetland, 69% secondary forest cover, and 15% rural land-use for Brandy Lake; 8% agriculture, 12% wetlands, and 65% secondary forest cover for Three Mile Lake, Persaud et al. (2014, 2015)).

Brandy Lake is a typical brown water lake stained with dissolved organic acids and comparably high DOC (Table 2). Brandy is the only study lake with a slightly acidic pH in the epilimnion (2015 summer measurements, Table 2). The lakes differ in some limnological characteristics (Table 2), but both have anoxic hypolimnia during summer stratification with elevated hypolimnetic TP concentration. Anoxic factors, computed from dissolved oxygen (DO) profiles as a measure of the extent of hypolimnetic anoxia (<2 mg/L DO) in space and time (Nürnberg, 1995), averaged 22 and 47 d/summer for Brandy Lake and Hammell's Bay of Three Mile Lake, respectively (Table S1). Summer internal loading computed from water TP increases was highly variable between years but averaged 52 and 59 mg/m² of Brandy Lake and Hammell's Bay surface area (Table S1).

Cyanobacteria blooms were reported routinely and consisted mainly of *Dolichospermum plancticum* (former *Anabaena planktonica*) in Hammell's Bay and *Aphanizomenon schindleri* in Brandy Lake (Persaud et al., 2014, 2015). A study of detailed algal, limnological and meteorological data found relationships with variables indicating internal P loading (hypolimnetic TP concentration and water stability) in these lakes (Persaud et al., 2015).

Different from the Sudbury area lakes, the comparison lakes did not show any long-term increase in summer TP concentration (Table 2, Jun-Sep epilimnetic TP mean ± SE. Brandy 1986–2014, n = 17: 24.5 ± 1.1 μg/L; Hammell's Bay 2006–2014, n = 6: 14.5 ± 0.4 μg/L, MOECC long-term data). Furthermore, lakes and streams less affected by the mining history have been found to have decreasing TP concentrations in south-central Ontario within the last three decades (Palmer et al., 2011; O'Brien et al., 2013).

2.2. Sediment sampling

Long Lake is extremely elongated and consists of basins of various depths that are separated by shallower bars, creating a chain of variously deep basins. Sediment cores were collected in two of these basins, at 20 m (Long3) and 22 m depth (Long5, Fig. S1) on June 7, 2015. Sediment cores from Brandy Lake and Three Mile Lake were collected at the deepest locations, which was at 7.5 m in Brandy Lake (May 19 and May 20, 2015) and 12 m in Hammell's Bay of Three Mile Lake (June 19, 2015, Fig. S1). Because it was early summer, none of these sites experienced hypolimnetic anoxia at the time of sampling.

Triplicate sediment cores were collected from Brandy Lake and Long Lake, and duplicate cores from Three Mile Lake (Hammell's Bay) using a

Glew gravity corer fitted with 60-cm Lucite core tubes (internal diameter = 7.62 cm). Core lengths varied between 12 and ~35 cm. Cores were extruded on site using a Glew extruder into two discrete sedimentary intervals: 0–5 cm and 5–10 cm. All sediment samples were stored in Whirl-pak® bags and refrigerated at 4 °C until processing for chemical analysis.

2.3. Sediment fractionation

To obtain some information about sediment history we examined 2 sediment layers in each core, 0–5 cm and 5–10 cm. In recent ²¹⁰Pb dating of 10 Sudbury area lakes, the 0–5 cm interval represented 37 (median, range 22–69) years of sedimentation and the 5–10 cm interval represented 73 (median, range 53–167) years (Tropea et al., 2010, 2011; Labaj et al., 2015). Assuming Long Lake sedimentation rates are similar, its 0–5 cm sediments may have accumulated within 0 to ~40 years during Phase 3 (Fig. 1), and its 5–10 cm sediment may have accumulated within about 40–110 years into the past and thus cover Phases 1 and 2 (Fig. 1). Mining operations started in the 1880s and signs of recovery from acidity in Sudbury area lakes were noted in the nineteen-seventies, about 40 years before the study (Nriagu et al., 1998).

The two sections of each collected core were each analyzed in triplicate. Water content and loss on ignition (LOI) were determined with standard methods by drying and igniting ~5.0 g aliquots of wet sediment samples at 103 °C (24 h) and 575 °C (2 h) respectively, to constant weight (Nürnberg, 1988). Total contents of P (TP), Fe (TFe), and Al (TAl) were determined from dried and ignited sediment after 24 h extraction by 1 N hydrochloric acid extraction (Ostrofsky, 2012). Samples were kept refrigerated until subsequent analysis.

Iron and aluminum bound P species were targeted specifically by the extraction methodology developed by Psenner (Psenner et al., 1984; Psenner and Pucsko, 1988) and since then used in many studies involving sediment P release and adsorption capacity (Nürnberg, 1988; Kopáček et al., 2000; Reitzel et al., 2006; Lake et al., 2007; Lukkari et al., 2007a, 2007b; Loh et al., 2013; Huser, 2017). In addition, Fe and Al were determined in these extracts because of their interactions with sediment P.

The extraction was performed on approximately 2 mL of wet sediment. In our first extraction step, sediment was incubated in a bicarbonate buffered dithionite (BD) solution containing 0.11 M sodium bicarbonate and 0.11 M sodium dithionite for 30 min at a temperature of 40 °C. This solution is effective in extracting pools of Fe bound phosphorus as reductant soluble P and Fe (Jan et al., 2013).

We did not separate Psenner's proposed first two steps, because Psenner's initial step involving H₂O or NH₄Cl determines the concentration of porewater P, which is typically very low (Nürnberg, 1988; Psenner and Pucsko, 1988; Lake et al., 2007) unless the sediments are extremely enriched as in a hypereutrophic lake (Hupfer and Lewandowski, 2005).

The second step employed a basic sodium hydroxide (NaOH) solution, effective in extracting Al-bound P, non-reducible Fe oxy-hydroxides, Al oxy-hydroxides and extractable Al in organic acids (Lukkari et al., 2007a). NaOH-P in softwater lakes mainly consists of Al adsorbed P (Jan et al., 2013). In productive lakes and coloured lakes some P may be associated with organic acids (Hupfer and Lewandowski, 2005). We determined the amount of humic P in the NaOH extraction by acidifying the extract (Reitzel et al., 2006) and found that it is <3% and 6% in Long Lake 0–5 and 5–10 cm layers, respectively, 0% and 2% in Three Mile Lake, and 0% and 3% in Brandy Lake despite its elevated colour. Although there may still be some P in fulvic and other dissolved organic acids we conclude that the proportion is small compared to Al-P compounds.

NaOH-Al is the main fraction that reacts with and permanently binds P in non-calcareous sediments (Kopáček et al., 2000). Besides aged Fe oxides and oxy-hydroxides not extracted in the BD step, NaOH-Fe indicates Fe from organic compounds in most non-calcareous lakes (Jan et al., 2015). A 25 mL aliquot of 0.1 M NaOH was added to each sediment

from the previous extraction step and exposed to continuous agitation for 16 h at room temperature. A 0.1 M NaOH concentration was used instead of the original 1 M NaOH solution of Psenner and Pucsko (1988), as recommended by Lukkari et al. (2007a) and used by others (Huser and Rydin, 2005).

All extractions included a washing step. Extracted P was determined as phosphate-P by standard MOECC analytical methods (Janhurs, 1998) based on the ascorbic acid and molybdenum blue method (Murphy and Riley, 1962). Some of the extracts were first exposed to acidic persulfate digestion to decrease interferences (necessary for NaOH-P) and yielded concentrations of total phosphorus (TP) of the extract. The differences between BD-P and BD-TP were 8–10% in the surface sediment and 6–11% in the deeper layer of the lake sediments. We here report only values for BD-P which is the fraction mostly involved in reductant P release (Psenner and Pucsko, 1988). Others have suggested that the difference (non-reactive P) is due to organic P compounds that may contribute to internal P loading in highly productive systems (Hupfer and Lewandowski, 2005), but is marginal compared to Fe hydroxide-associated P (BD-P) in less eutrophic lakes (Amirbahman et al., 2012) such as ours.

The solubilized Al and Fe concentrations were determined by microwave plasma (MP) with atomic emission spectroscopy (Agilent 4200 MP-AES).

Reproducibility in the triplicate sediment analysis of the same core was generally quite good and lower than variability between cores taken from the same site (see next). Precision expressed as relative standard error (SE in % of mean) of triplicate analysis was <3.2% on average for P (BD-P, NaOH-P and TP) similar to earlier studies (Nürnberg, 1988), <4.6% for TFe and BD-Fe, but up to 11.4% for the small concentrations of NaOH-Fe, <5.0% for NaOH-Al and TAl, but up to 7.5% for the small concentrations of BD-Al.

In comparison to the analytical variance, variability between cores (SE in % of mean of 2 or 3 cores) was slightly larger. It was <7.2% on average for P (TP, BD-P, and NaOH-P), <8.4% for TFe and BD-Fe, but up to 13.6% for the small concentrations of NaOH-Fe, <6.7% for TAl, but up to 11.8% for the BD-Al and NaOH-Al.

2.4. Data analysis

We reported mean and SE to show the differences between depth layers and sites of sediment fractions and their ratios. (The 95% confidence interval extends approximately twice the SE around the mean.) We also used t-tests for more direct tests. Significance levels (p) were reported to levels of 0.05, and 0.01. For small sample sizes we report p values between 0.05 and 0.10 as well. Pearson regression analysis was used to test for relationships. All reported statistical analyses, including the box and whisker plots and outlier analysis, were done with the SYSTAT statistical program, version 13 for Windows.

3. Results and discussion

Because of possible post-diagenetic migration of P and Fe, concentrations in the deeper sediments have to be carefully interpreted. On the other hand, Al components are not involved in post-diagenetic migration but mostly represent accumulation from settling and subsequent burial (Carignan and Nriagu, 1985). We computed molar ratios for both sediment layers, the surficial 0–5 cm and the deeper 5–10 cm layer, because these ratios describe the relationships between Al, Fe and P within the specific sediment layer even after post-diagenetic migration (in the 5–10 cm layer). We assume that patterns in these ratios may help indicate sediment adsorption capacity variation, especially when involving Al and the Al dominated NaOH fraction.

The comparably low nutrient state of the study lakes and the dilute concentrations of many of the involved substances, especially of BD-P, has to be considered when interpreting results as they may make it difficult to prove statistically significant relationships. We suggest that

more such studies be completed in mining areas to confirm these results. Also, the analysis of smaller intervals of sediment profiles, preferably dated by ^{210}Pb , would provide a more detailed historic development of such lakes.

3.1. Sediment total concentrations and fractions of P, Al, and Fe

Average sediment concentrations of the cores for each site are presented in combination with SE to provide a simple evaluation of variability (Table S2, Table S3). Brandy Lake surface LOI is highest, as expected in this lake stained with humic and fulvic acids, and indicates the presence of organic material in its sediment.

Long Lake sediment at the upstream station Long3 had consistently higher concentrations of P, Al, and Fe compared to Long5 (Fig. 3). As water content was similar (Table S2), this result can be explained from the relative locations of the sites along the flow of Long Lake (Fig. S1). External material input is being deposited in the basins along the lake bed. At both stations, P and Al compounds tended to be higher in the deeper sediment layer, which may be related to Long Lake's mining history as described below.

Long Lake sediment TP concentration was similar to that of the non-mining study lakes [and similar to other Muskoka lakes (Nürnberg, 1988)] in both depth layers (Table S3). Of all tested sediments, 5–10 cm BD-P was significantly lower at Long5 and was also lower at Long3

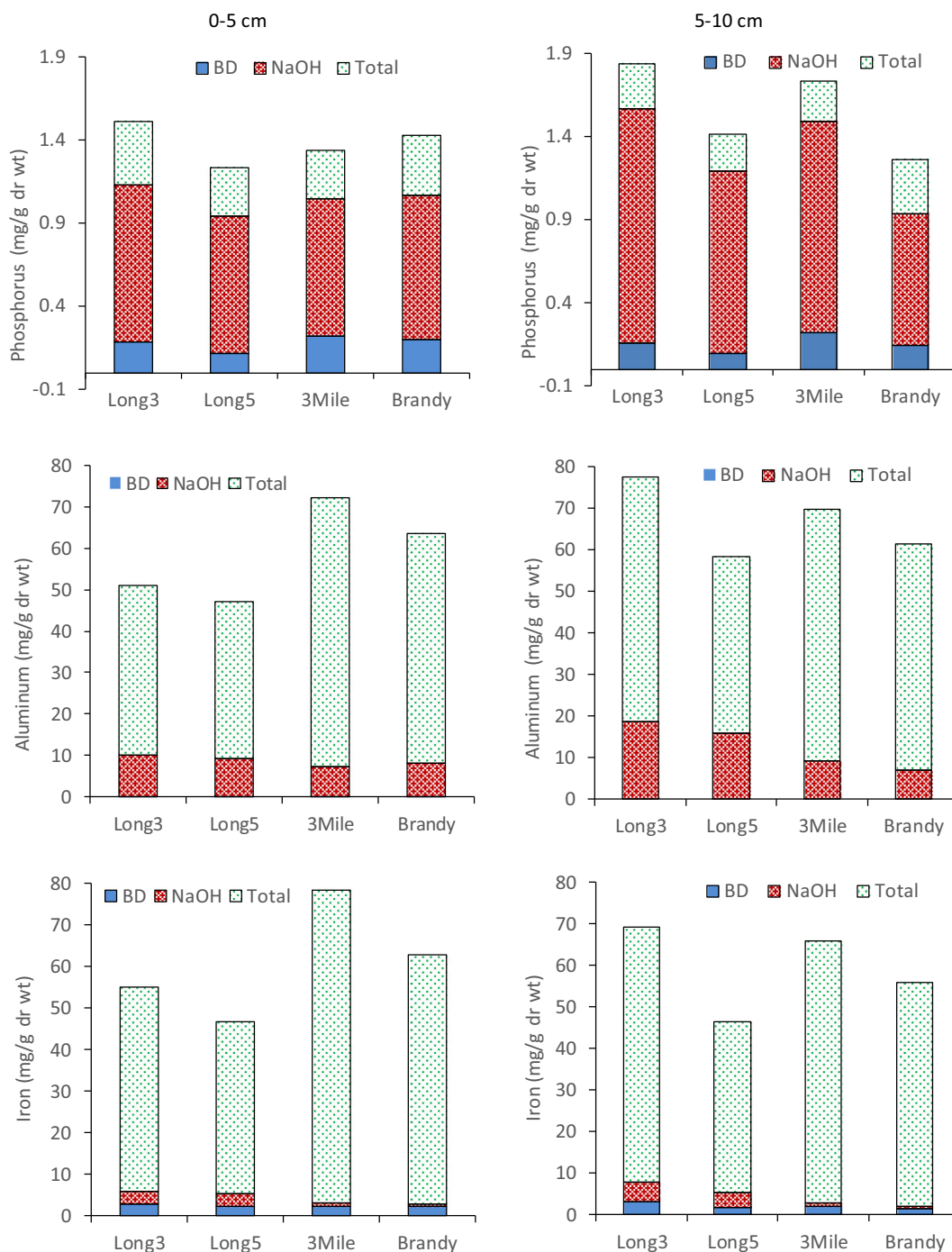


Fig. 3. Sediment concentration of reductant-soluble (BD) and organic/Al fractions (NaOH) of the total element (entire bar) of P, Fe and Al in 0–5 cm (left column) and 5–10 cm (right column) sediment layers of the study lakes. Mean of 3 cores each for Long Lake sites and Brandy, and 2 cores for Three Mile are presented (data from Table S3).

than surface BD-P; most Long Lake BD-P concentrations were lower than in the non-mining lakes for both sediment layers. Lower BD-P means less potential for anoxic sediment P release (Nürnberg, 1988; Kopáček et al., 2005; Lake et al., 2007) in comparison to the more nutrient rich non-mining lakes, as is expected in the past for acid lakes (Phase 2, Fig. 1, Kopáček et al., 2015).

We determined a significant relationship between BD-P and TP in the surface sediment layer for all lakes, and noted that the 5–10 cm layer is following the same trend for the non-mining lakes, but not Long Lake cores (Fig. S3). Such significant regressions have been reported for other non-acidified and non-mining lakes in eastern North America before (Nürnberg, 1988).

NaOH-P was highest in the Long and Three Mile Lake 5–10 cm sediment layers, while surface sediment NaOH-P concentrations were similar in all lakes (Fig. 3). Higher NaOH-P is associated with more P adsorbed by Al as is expected in the past of formerly acid lakes (Kopáček et al., 2005, 2015; Jan et al., 2015). NaOH-P was not significantly correlated with BD-P in either sediment layer.

TFe and TAl were slightly lower in Long Lake 0–5 cm layer compared to the non-mining lakes (Table S3, Fig. 3). Deep layer TAl and NaOH-Al concentrations were significantly higher than 0–5 cm layer concentrations in Long Lake. In contrast, TAl was not significantly different between the two depths in the non-mining lakes, and deep layer NaOH-Al was significantly higher only in Three Mile Lake, while it was significantly lower in Brandy (Table S3, Fig. 3). As expected, the BD extraction does not extract a considerable amount of Al and the BD-Al concentrations are close to the detection limit in all study sediments.

Elevated TAl and NaOH-Al concentrations in the older, 5–10 cm, sediment layer in Long Lake can be explained by its acid mining history that was associated with high Al export from the watershed during Phase 2 (Fig. 1). During the period of increasing buffer capacity in the watershed and increases in lake pH, Al export and Al lake concentration decreased (Table 1), impoverishing the previously abundant sediment Al pool to that of the non-mining lakes (Phase 3, Fig. 1). Such Al decreases have been reported previously in other formerly acid-stressed or nutrient-poor lakes (Section 3.3).

BD-P tended to be negatively correlated with NaOH-Al except in the deep Long Lake sediment layer (Fig. S4), which can be explained by post-diagenetic changes or extraction artifacts as discussed in SI. In Long Lake deep sediment, BD-P appeared to be more controlled by iron as discussed next.

BD-Fe concentration was similar in all surface sediments and while no significant differences were detected between depths, they tended to be higher in the surface layer except in Long3 (Fig. 3). BD-P was positively correlated with BD-Fe but only in the deep sediment layer and excluding the non-mining lakes ($R^2 = 0.714$, $n = 5$, $p = .071$). Such a correlation indicates that both, P and Fe are extracted by the BD solution as theoretically expected. Since it was only observed in sediments where BD-P was not significantly negatively correlated with NaOH-Al (Long Lake deep sediments, Fig. S4) this may indicate conflicting control on BD-P, potentially complicated by the diagenesis of sediment after burial that typically causes upward migration of Fe to surface sediment (Norton et al., 2008) and extraction artifacts causing P adsorption deliberated from BD extraction by Al in the NaOH extraction (Fig. S4). In all 11 cores, except for two collected from site Long3, BD-Fe was lower in the deep sediment layer. We point out that the small sample size and the very low concentration of BD-P compared to BD-Fe may influence these relationships.

The Long Lake NaOH-Fe fractions were more than three times that of the non-mining comparison lakes (Fig. 3). NaOH-Fe is usually thought to originate from organic compounds (Jan et al., 2013) but the elevated concentration in Long Lake is more likely to originate from dissolving FeS that is high in lakes with acid deposition enriched in sulfate (Carignan and Tessier, 1988), especially since organic sediment content (LOI) was not significantly different between the lakes.

3.2. Indicators of sediment P retention trends

3.2.1. Al:P ratios and NaOH-P proportion

We used established ratios of Al versus P concentrations in the Psenner-based BD and NaOH extracts to assess the P retention capacity of the lake sediments. Specific thresholds for several ratios indicate the likelihood of P adsorption versus P release in sediments (Rydin et al., 2000; Kopáček et al., 2005; Huser and Rydin, 2005; Huser, 2017), where higher ratios indicate higher P retention capacity.

The NaOH-Al:BD-P ratio (threshold: molar = 25, weight = 22) was hypothesized to determine the P adsorption capacity of sediments in Central European lakes, but a large range of ratios up to 1981 were reported in oligotrophic sediments (Kopáček et al., 2005). The NaOH-Al:BD-P ratios were above the molar threshold of 25 in all of our study lakes and depths. Both ratios were significantly higher in the deeper sediment layer in Long Lake compared to the surface layer and were also much higher than in the non-acid study lakes (Fig. 4), which supports our hypothesis of recently decreased sediment adsorption capacity (Phase 3, Fig. 1). But the much higher ratios than 25 in the non-mining lakes with evidence of sediment P release as internal loading (Table S1) indicates that the exact threshold value may not apply in different systems or where slightly different analytical methods are used (see also, Loh et al., 2013). We therefore focus on the trend of the ratio value between sediments.

We also examined a NaOH-Al:NaOH-P threshold based on experience from Rydin et al.'s (2000) lake restoration treatments. In six lakes previously treated with Al sulfate (Alum) a NaOH-Al:NaOH-P ratio of 12.6 M (11.2 by weight) (Rydin et al., 2000) was determined. As these lakes apparently were successfully treated (ceased internal loading), the Al concentration must have been high enough for the total adsorption of releasable sediment P, including that migrating from below the treated layer.

More recently formed Al hydroxides have higher adsorption capacity than those from older applications. Therefore, studies determined a range of molar ratios between 5.6 and 14.5 from Danish and USA lakes down to an unusually low value of 2.1 in a small Minnesota lake (Huser, 2017). This low ratio was stable in the deep sediment after Al translocation from the shore where Al was applied, but P release increased to pre-treatment levels after 10 years (Huser, 2017).

Surface sediments of all study lakes had NaOH-Al:NaOH-P ratios at or below the threshold of older Alum applications, which is a supporting indicator of low retention capacity and probable sediment release (Fig. 4). Only Long Lake 5–10 cm layer had ratios significantly exceeding this threshold (significant differences between depth layers, Table S3) indicating high retention capacity in sediments during its acidified past (Phase 2, Fig. 1).

Three Mile Lake deeper sediment NaOH-Al:NaOH-P ratio was significantly lower than its surface sediment, but NaOH-Al:BD-P was significantly higher, yielding conflicting trends in this lake with respect to P retention. This could be attributed to the small sample size of only 2 cores for this site. There were no significant depth differences in Brandy Lake sediment layers with respect to both ratios (Fig. 4), which is expected from a lake without a mining history.

We also examined the simple ratio of NaOH-P:TP because it indicates the proportion of sediment P that is extractable by NaOH and therefore associated mainly with Al. This ratio was significantly higher in Long Lake deep sediments (Table S4) indicating enhanced Al-P in older sediments, while it was similar in all surface sediments. This ratio was inversely correlated with epilimnetic pH in European lakes so that a pH of 6 coincided with a ratio of 0.8 (Kopáček et al., 2005), which is close to the ratio determined for the Long Lake 5–10 cm sediment layer. The recent Long Lake pH of 7.1 (Table 2) and the 0–5 cm average sediment ratio of 0.64 (Table S4) compare well to the trend observed by Kopáček et al. (2000), further supporting Long Lake recuperation from acidity and associated decrease in Al adsorbed P.

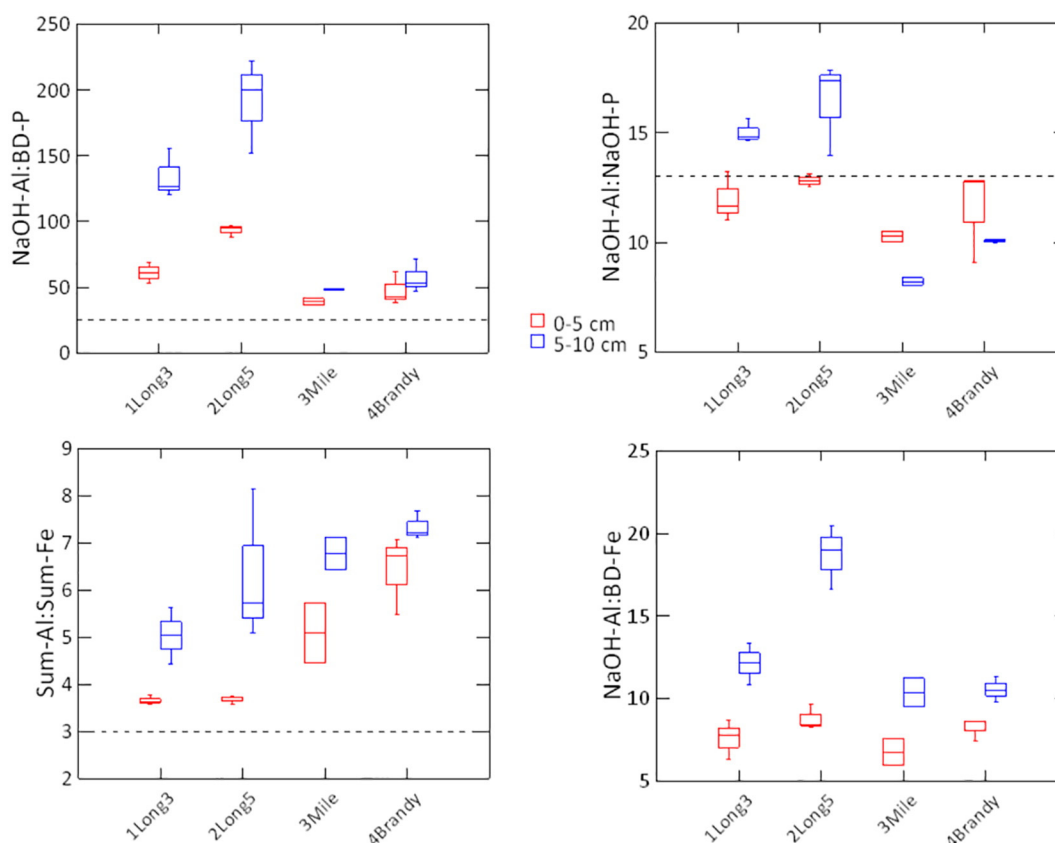


Fig. 4. Molar ratios of Al:Fe and Al:P in 0–5 cm and 5–10 cm sediment layers of the study lakes (for means and standard errors presented in Table S4). Higher ratios mean more retention capacity. Thresholds for ratios that favour P retention observed in other studies are indicated. Box and whisker plots of 3 cores each for Long and Brandy sites and 2 cores for Three Mile are presented. The lower and upper boundaries of the box plot represent the 25th and 75th percentile, respectively. The lower and upper whiskers represent the 5th and 95th percentile, respectively.

3.2.2. Al:Fe ratios

Kopáček et al. (2005) determined that a molar ratio of Al to Fe above 3 in the sum of three extracts (NH_4Cl , BD and NaOH, Psenner and Pucsko, 1988), which represents the first two extracts in our study, would indicate a high sediment adsorption capacity by Al and only limited P release. Subsequent studies determined similar patterns and thresholds based on BD-Al, NaOH-Al and BD-Fe (and an initial NH_4Cl extraction, which is included in our BD extraction) (Lake et al., 2007). Their threshold ratio lay between 2 and 4. The actual number 3 is not necessarily applicable in this study, because of slightly different methods (e.g., Kopáček et al., 2005 and Lake et al., 2007 used 1 M NaOH in the NaOH extraction step, Section 2.3), different sediment characteristics and water conditions such as a much lower trophic state. Nonetheless, a downward trend in this ratio should indicate decreased P retention capacity.

The surface ratios in Long Lake were 3.7 at both sites and thus approached the Kopáček threshold of 3 under which P retention capacity is supposed to be limited. Long Lake ratios were up to 80% higher in the deeper sediment layer which was significant at Long3 and the combined sites, but differences between layers were less and not significant in the non-acid lakes (“Sum extracted Al:Fe ratio”, Fig. 4). Our non-mining, P releasing lakes exhibited higher ratios at 5.1 and 6.4, not conforming to the theory of P retention, which may be due to different characteristics, at least for humic Brandy Lake that is enriched in DOC (Table 1).

Kopáček et al. (2005) observed that the Al:Fe ratio in the sum of the three extracts was significantly negatively correlated with BD-P for non-acid lakes surface sediment, while acid lakes had low BD-P for a range of Al:Fe ratios. These findings are partially supported by this study despite

the much lower trophic state of our lakes. There is a significant negative relationship for the 0–5 cm sediment ratios of the non-mining study lakes when one influential outlier is omitted ($R^2 = 0.97$, $p < .05$, $n = 4$), but in Long Lake the ratio is almost constant at the low value of 3.7 (Fig. 5, Table S4).

We also determined the ratio of just two fractions, NaOH-Al and BD-Fe, because these extractions may be most specific to characteristics involving P retention. The NaOH extraction is specific for Al that is involved in adsorbing P (NaOH-P) and the BD extraction is specific to Fe that is involved in the release of P (BD-P) from iron-oxo hydroxides. This ratio does not consider the NaOH-Fe, which is uncommonly high in Long Lake (as high as BD-Fe, Fig. 3) compared to the non-mining study lakes and lakes in Maine (Lake et al., 2007), but similar to Plešné Lake (central Europe) (Kopáček et al., 2005). This ratio is more similar to that used by Lake et al. (2007), who also omitted the NaOH-Fe fraction but included the BD-Al portion.

Long Lake NaOH-Al:BD-Fe ratios in the deeper sediment layer were significantly and close to two times higher than in the surface layer and also higher than in the deep layer of the non-acid lakes (“NaOH-Al:BD-Fe”, Fig. 4). In comparison the surface ratios were not significantly different among the lakes indicating that Long Lake sediment is approaching the retention capacity of the less P-retaining, non-acid lake sediments (Phase 3, Fig. 1). Because the values of the NaOH-Al:BD-Fe ratios reveal conspicuous differences between the study lakes and sediment depths, we propose to further investigate whether they can serve as a threshold similar to the ratio of the sum of extracted Al:Fe (Kopáček et al., 2005). Based on the values of the NaOH-Al:BD-Fe ratios, we propose that the highest ratio (10–11) of the non-mining lakes with internal loading histories

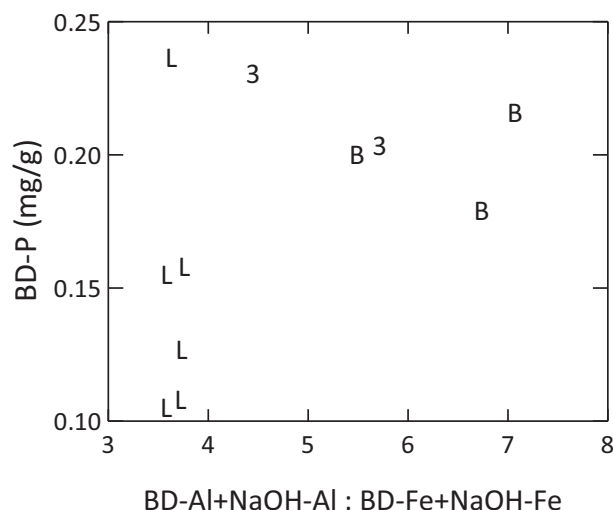


Fig. 5. Surface (0–5 cm) BD-P versus (BD-Al + NaOH-Al) : (BD-Fe + NaOH-Fe), the Al:Fe ratio in the sum of the BD and NaOH extractions. Symbols represent lake names (Table 2).

determines the sediment P adsorption capacity that is high enough to prevent P release from anoxic sediments.

3.3. Comparison with trends in acid and non-acid lakes, worldwide

Throughout this study, we found that observations and conclusion from the well-studied central European region affected by acid deposition (Kopáček et al., 2000, 2005, 2006, 2015) are applicable to the Sudbury area lakes despite the generally higher trophic state and water TP concentration in Europe. Similarly, Swedish studies support our findings. A substantial portion (up to 76%) of the total external P load was converted to P adsorbed by Al (NaOH-P) and buried in the sediment over the period 1950–2001 of industrial acidification in two Swedish Lakes (Huser and Rydin, 2005). Sulfate in precipitation was positively and significantly correlated with NaOH-P. Sulphur dioxide emissions from the Sudbury area smelters were elevated from 1960 to 1972, declined to a medium level in 1983–1990 and then to a lower level in 1993–2000 (Keller et al., 2004). The significantly lower Al (total and NaOH-Al) and NaOH-P levels in Long Lake 0–5 cm sediment (Fig. 3) can be explained by decreasing acidification due to declines in sulphur dioxide emissions. These fractions were less depth dependent in Three Mile and Brandy Lake and similar to Long Lake 0–5 cm sediment (Fig. 3).

Also, the lake restoration technique of the addition of Al salts for internal load abatement is based on P adsorption by Al and the transformation of BD-P into NaOH-P (James, 2017; Huser, 2017).

Sediments in less acidic (pH = 6–7) lakes in Maine exhibit characteristics comparable to the sediment of the non-mining study lakes. For example, nutrient-poor lakes with “low internal load of P to the water column” usually had (BD-Al + NaOH-Al):(BD-Fe) and NaOH-Al:BD-P ratios exceeding the Kopáček thresholds, although not all lakes with lower ratios exhibited internal loading (Lake et al., 2007; Norton et al., 2008; Wilson et al., 2008; Amirbahman et al., 2012). While these lakes did not have an acidification history their P retention was influenced by photo-oxidation and liberation of Al and Fe from DOC compounds for >150 years (Norton et al., 2008). We expect that organic-acid stained Brandy Lake may experience similar processes.

In addition to decreases in acid deposition, a trend of decreasing Al related to temperature increases was described in Czech lakes recovering from acidification (Vesely et al., 2003). The inverse relationship between Al solubility and temperature caused lower Al mobilization in soils and possibly reduced settling of Al in lakes at higher temperature. Temperature increases have also been observed in the Sudbury area, potentially causing increased stratification, earlier ice out, and internal P recycling (Sivarajah et al., 2016). Temperature trends related to climate

change may support the Al decreases in water and recent sediments observed in this study; they may also increase thermal stability (Hadley et al., 2014) and enhance intensity and duration of hypolimnetic hypoxia and internal P loading.

Our results support the observations (Table 1) that lakes recovering from mining activities show increasing productivity and trophic state and do not exhibit P decreases as recently observed in non-mining Ontario (Stammiller et al., 2017), Finnish (Arvola et al., 2011), and Swedish lakes (Huser et al., 2018). Declining stream P concentrations resulting in reduced external loads to receiving lakes as reported in undeveloped headwater streams (Eimers et al., 2009) are unlikely in the Sudbury area.

3.4. Potential effect on cyanobacteria proliferation

We suspect that increases in cyanobacteria (mostly *Dolichospermum*) and their recent blooms in Long Lake are directly related to the decreased sediment P adsorption capacity and resulting release of phosphate during periods of summer hypolimnetic anoxia. While *Dolichospermum* in Long Lake may also be reinforced by temperature increases from climate change, a study on >1000 lakes found *Dolichospermum* to be more dependent on P in oligotrophic lakes, and *Microcystis* (not identified in Long Lake) more dependent on temperature (Rigosi et al., 2014). Significant increases in cyanobacteria blooms in other Ontario lakes including acid-stressed lakes on the Canadian Shield, were also partly explained by climate warming effects, including a lengthening of the stratification period (Winter et al., 2011), which would support internal P loading.

Observations in highly alkaline oligomictic Lake Winnipeg (Nürnberg and LaZerte, 2016), in stratified and mixed basins of Lake Simcoe (Nürnberg et al., 2013), and in a eutrophic bay of Lake Champlain, where redox-related P concentrations were correlated with cyanobacteria cell counts (Smith et al., 2011), concur with observations on the potential of internal P loading to increase harmful cyanobacteria blooms (O’Neil et al., 2012). Also, a meta analyses on lakes world-wide concluded that the proportional increase of cyanobacteria was explained best by nutrient concentration and secondarily by temperature (Taranu et al., 2015). Further, the effects of internal loading on cyanobacteria blooms is implied within various studies and suggestions to address internal load management as a potential approach to reduce such blooms (Paerl et al., 2011; Lindim et al., 2015; Nürnberg, 2017).

4. Conclusions

Sediment fractions containing P, Al, and Fe compounds for two sediment layers suggest that the acid-affected sediments have been buried in the 5–10 cm layer of oligotrophic Long Lake, which is recuperating from acid-deposition. Meanwhile, the surface sediment layer P, Al, and Fe relationships have become more similar to those from regional mesotrophic lakes with known P release as internal loading. We conclude that the water quality changes in Long Lake are a consequence of recovery from acidity during ongoing P inputs from development and under conditions of climatic change. Decreases in the Al hydroxide-based sediment adsorption capacity and P retention in anoxic sediments are the primary factors in this recovery.

There is cause for concern that increased eutrophication including the proliferation of cyanobacteria of formerly acidic lakes is widespread and occurs wherever recovery coincides with anthropogenic disturbances and physical changes related to climate change.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.01.103>.

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